

PATENT SPECIFICATION

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Inventors: JOHN SCOTCHFORD ELLIOTT, ERIC DESCAMP
EDWARDS and GERALD JOHN JOSEPH JAYNE

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COMPLETE SPECIFICATION

Additives for Lubricating Compositions

We, CASTROL LIMITED, a British Company, of Castrol House, Marylebone Road, London, N.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

The invention relates to additives for lubricating compositions and also to lubricating compositions containing the additives. In particular, the additives with which this invention is concerned are detergents which are effective cold sludge dispersants.

In the lubrication of modern internal combustion engines deposits may be formed in the engines in two ways and there are two distinct problems involved in keeping the engines clean. One problem is the deposition of soot, lacquers and other deposits, mainly in the piston ring zone, under high speed, and consequently high temperature, operating conditions. These deposits may arise from partial combustion products of the fuel or as the result of the oxidation or thermal degradation of the lubricant or both. This problem is alleviated by the addition to the lubricating oil of what are known in the art as high temperature detergents, conventional detergents or normal detergents. The other problem is the deposition of another kind of "dirt". This "dirt" has become known as "cold sludge". Cold sludge is formed in engines in cold weather and under driving conditions obtaining in cities and in other conditions when the engines never truly warm up. This latter problem is alleviated by the addition to the lubricant of additives known as cold sludge dispersants. "Cold sludge" is derived almost entirely from the fuel and is normally wet.

In the past the conventional detergents have in general been metal containing derivatives of organic compounds such as basic alkaline earth metal petroleum or alkyl benzene sul-

phonates, basic alkaline earth metal salts of phosphosulphurised polybutenes or alkaline earth metal phenates. The cold sludge dispersants, on the other hand, have in general been copolymers of polar monomers such as N-vinyl pyrrolidone with oil-solubilising copolymerisable monomers such as long-chain alkyl methacrylates.

More recently, products having useful detergent and cold sludge dispersant properties have been obtained by reacting a long chain substituted succinic anhydride, preferably polyisobutenyl succinic anhydride, with polyamines such as polyethylene polyamines or β -amino piperazine.

According to the present invention there is provided a novel additive for lubricating compositions which is an oil-soluble chromate or molybdate salt of the reaction product of a long-chain substituted succinic acid or anhydride and a di- or poly-amino compound containing at least one primary amino group, said long-chain substituent being a hydrocarbon group having a molecular weight of at least 700 and said reaction product containing at least one basic nitrogen group.

This invention also includes a lubricating composition comprising a major proportion of a lubricating oil and a minor proportion, sufficient at least to provide the desired degree of cold sludge dispersancy and detergency, of the said salt.

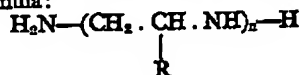
The long chain substituted succinic anhydride may be obtained from the reaction between a normally liquid oil-soluble polyolefin having a molecular weight of from 700 to 3000, preferably from 750 to 1500, and maleic anhydride. Preferably the polyolefin is polyisobutylene.

It is believed that the long chain substituent obtained in this manner will generally contain an average of one ethylenically unsaturated bond. However, this unsaturated bond may be subsequently hydrogenated. It is believed that the saturated compounds have substantially

[Pric

similar properties to the unsaturated compounds. It will be appreciated therefore that the long chain substituent may be saturated or unsaturated.

- 5 Suitable di or polyamino compounds which are reacted with the long-chain substituted succinic acid or anhydride are amines having the formula:



- 10 wherein R is H or an alkyl radical having from 1 to 6 carbon atoms per molecule and n is an integer of from 1 to 8 or more. Specific examples of such amines are ethylene diamine, diethylene triamine, triethylene
15 tetramine, tetraethylene pentamine, pentaethylene hexamine and mixed higher polyethylene polyamines.

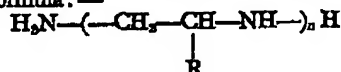
- Alternatively, amines such as N-amino alkyl piperazines, or N-dialkyl amino alkyl amines, such as N-dimethyl amino propyl amine, may
20 be employed if desired.

- Other suitable di or poly amino compounds are those obtained by reaction between polyalkylene polyamines in which the number of
25 alkylene groups per molecule is at least 2 such as primary alkylene polyamines having at least two primary amino groups and contain-

ing the group $-\text{NH}-(\underset{|}{\text{C}})_A\text{NH}_2$ where

- A is from 2 to 4 and γ -lactones, especially
30 γ -butyro lactone or γ -valero lactone, or dicyandiamide, otherwise known as cyanoguanidine, as disclosed in our co-pending patent applications Nos. 36965/63 and 28456/64 (Serial Nos. 1,054,370 and
35 1,068,235).

- In a particularly preferred aspect of the invention the di- or poly- amino compound is the reaction product of a polyamine having
40 the formula:—



- where n is an integer of from 2 to 8 and R is H or an alkyl radical having from 1 to 6 carbon atoms, with γ -butyro lactone or γ -valero lactone. In a further particularly preferred aspect of the invention the di- or polyamino compound is the reaction product of dicyandiamide with a primary alkylene polyamine having at least two primary amino groups and containing the group
45



where A is from 2 to 4.

Suitable starting materials are the products obtained by simply heating, with stirring, a mixture of the long chain substituted succinic acid or anhydride and the di- or polyamino compound at a suitable temperature and for a suitable time, optionally in a solvent, until the product is substantially all succinimide as determined by infrared analysis. Typical reaction conditions are, for example, heating in toluene for 6—8 hours followed by removing all the solvent by distillation; or, preferably, heating the reactants in about 50% by weight of mineral oil at about 200° C for 4 hours. If desired, these starting materials may be further reacted with carboxylic acids to give imidazolines.

The additives of this invention are conveniently prepared by heating a mixture of an oil concentrate of the succinic anhydride/di or polyamino compound reaction product as herein defined and the appropriate oxide or acid or ammonium salt at a temperature, for example, between approximately 80° and 100° C in the presence of water.

The molar ratio of the succinic anhydride/di- or polyamino compound reaction product to the appropriate inorganic oxide or acid or ammonium salt may vary from 1:1 to 6:1, preferably from 2:1 to 4:1.

The lubricating compositions of this invention may exhibit adequate cold sludge dispersancy and high temperature detergency by the incorporation therein of quite small amounts of the additive, and the compositions may contain, for example, 0.5 to 10% by weight of the additive, and, preferably, from 1.0 to 5.0% on the weight of the composition. However, in some cases, particularly in the case when a lubricating oil concentrate is required, it may be desirable to use concentrations greater than 10%.

It is to be understood that the lubricating compositions of the present invention may contain also copper deactivators, pour-point depressants, antioxidants, viscosity index improvers and other conventional additives as necessary.

Particularly preferred antioxidants which may be used in conjunction with the additives of the present invention are the metal salts of dialkyl or di(alkaryl) dithiophosphoric acids, especially the zinc salts of dialkyl dithiophosphoric acids derived from C_2 — C_{10} alcohols. The dithiophosphate may be present in the composition in amounts of from 0.2 to 2% and preferably of from 0.5 to 1.5% by weight based on the weight of the composition.

There now follows by way of example a description of the preparation of a typical additive and of a lubricating oil composition according to the present invention.

EXAMPLE 1

The preparation of polyisobutenyl succinic anhydride

- (1) 330g. (0.3 mole) of a polyisobutylene of average molecular weight 1100, 32.34 g. (0.33 mole) of maleic anhydride and 5.82 g. (0.04 mole) of di-*t*-butyl peroxide were refluxed with stirring in 210 mls. of toluene, in a 2-litre flask fitted with thermometer pocket, nitrogen inlet, condenser and rotational stirrer, for 30 hours. The toluene was distilled off and 210 mls. of hexane added, whereupon unreacted maleic anhydride was precipitated and this was removed by filtration using a filter aid. The hexane was distilled off and the product vacuum stripped for 1 hour at 200° C. and 10 mm.Hg. pressure. The product was again filtered through a steam-heated filter funnel to yield 296 g. of a clear brown product. The purity of the product was determined by saponification. The saponification value was 73.5 mg. KOH/g (calculated=93.5). The product therefore contained about 79% of polyisobutenyl succinic anhydride together with 21% of unreacted hydrocarbon.

- (2) A similar product was obtained by stirring 1395 gm. (1.33 mole) of polyisobutylene of average molecular weight 1050 with 143.7 gm. (1.463 mole) of refluxing maleic anhydride and, when the reflux level dropped, heating to a temperature of 240—250° C. for a further 20 hours. The reactants were allowed to cool, 1 litre of hexane added and the solution filtered through a diatomaceous filter aid. The hexane was distilled off and the product vacuum stripped for 2 hours at 200° C. and 10 mm. Hg. pressure. 1397 gm. of a clear viscous liquid was obtained.

Saponification value of product=77.5

This product therefore contained 79.5% of polyisobutenyl succinic anhydride.

- Reaction between triethylene tetramine and dicyandiamide

- 730 g. (5 mole) of triethylene tetramine and 420 g. (5 mole) of dicyandiamide were placed in a 1 litre flask equipped with stirrer, nitrogen bleed, reflux water condenser and internal thermometer and the temperature slowly raised. At 110—120° C the mixture became clear and at 150° C ammonia was evolved, whereupon the heat source was removed until the evolution of ammonia had died down. At this stage a solid began to crystallise which dissolved on further heating to 280° C. The mixture was maintained at this temperature for four hours, the total period of heating being 8 hours. The product was a red-brown brittle glass which was hygroscopic and was found to contain 40.5% Nitrogen.

Reaction between polyisobutenyl succinic anhydride and the reaction product of triethylene tetramine and dicyandiamide

Intermediate B

A mixture of 2026 g. of a polyisobutenyl succinic anhydride of approximately 85% purity prepared as above from polyisobutylene of MW ca 1050 and 319.5 g. of the reaction product of triethylene tetramine and dicyandiamide obtained as described above was stirred for 8 hours at 200° C with the passage of nitrogen. On cooling to 120° C the product was diluted with 2292 g. of mineral oil and filtered through a steam-heated filter.

Preparation of a chromate salt of the reaction product thus obtained

310 g. of the reaction product thus obtained, 5.0 g. (0.05 mole) of chromium trioxide and 40 mls. of water were stirred in a one litre flask at 100° C. for 3 hours under a reflux condenser. After this period the reflux condenser was removed and the temperature raised to 150° C. with the passage of nitrogen to remove the water. The product was filtered through a steam-heated funnel and analysis showed that it contained 0.20% Cr and 2.20% N.

EXAMPLE 2

Reaction between polyisobutenyl succinic anhydride and tetraethylene pentamine.

Intermediate A

433.5 g. (0.3 mole assuming 79.5% purity) of a polyisobutenyl succinic anhydride prepared by the method of Example 1 (2) and 56.7 g. (0.3 m) of tetraethylene pentamine were heated in a nitrogen atmosphere for 4 hours at 200—220° C, during which time water was evolved. After vacuum stripping for 1½ hours the product was found to contain 3.78% Nitrogen.

Preparation of a molybdate salt of the reaction product thus obtained

81 g. (0.05 moles) of the reaction product thus obtained and 3.58 g. (0.025 moles) of molybdenum trioxide were heated with vigorous stirring with 20 mls. of water. No emulsion was formed and therefore 83 g. of mineral oil were added, whereupon an emulsion was formed. This emulsion was heated at 100° C. for 3 hours under a reflux condenser with continuous stirring. The condenser was then removed and the temperature raised to 110° C. with the passage of nitrogen to remove the water. The product was very viscous and was therefore further diluted with 166 g. of mineral oil to give a 25% concentrate which, on filtering through a steam-heated funnel, was found to contain 0.76% Mo and 0.92% N.

The details of further examples of preparations according to the present invention are given in Table I. These were prepared in substantially identical manner to Example

I or Example II any differences being explained in the comments following the table. The mineral oil used throughout was a light spindle oil having a viscosity at 140° F of 52 Redwood 1 seconds. All the intermediates, unless otherwise stated, were employed as 50% concentrates in mineral oil, the weights relating to the concentrate and not to the neat compound. Those cases where neat intermediates were employed are marked with an asterisk. In some cases further oil was added subsequently, this being indicated by a dash.

TABLE I

Example No.	Intermediate		Source of Anion		Analysis of Product			Water used in reaction (mls)	Mineral Oil Added (g)	Final Concentration % by weight
	Inter-mediate	Wt. (g)	Moles	Source of anion	Wt. in g	Moles	% Metal	% N		
3	A	153	0.05	CrO ₃	5.0	0.05	0.61	1.63	40	50
4	A*	81	0.05	CrO ₃	2.4	0.025	0.56	1.73	20	50
5	A*	91	0.05	CrO ₃	1.25	0.0125	0.57	—	—	neat
6	A	153	0.05	MoO ₃	7.2	0.05	1.87	0.93	40	25
7	A	306	0.1	(NH ₄)MoO ₃	20.6	0.0166	1.87	1.03	40	25
8	A	306	0.1	MoO ₃	7.2	0.05	1.21	1.21	40	25
9	A	153	0.05	H ₂ MoO ₄	4.0	0.025	0.92	0.83	40	25
10	A	153	0.05	MoO ₃	2.4	0.0167	0.48	0.80	20	25
11	A	153	0.05	MoO ₃	1.80	0.0125	0.90	1.64	20	50
12	B	155	0.05	CrO ₃	5.0	0.05	1.32	2.1	20	50
13	B*	92.25	0.05	CrO ₃	1.25	0.0125	0.66	—	20	neat
14	B(1)	86	0.0125	CrO ₃	0.312	0.00312	0.22	1.40	20	50

TABLE I (Continued)

Example No.	Intermediate	Source of Anion			Analysis of Product			Water used in reaction (mls)	Mineral Oil Added	Final Concentration
		Wt. (g)	Moles	Source of Anion	Wt. in g	Moles	% Metal	% N		
15	B	310	0.1	MoO ₃	7.2	0.05	0.79	1.09	320	25
16	B(2)	58	0.025	MoO ₃	0.9	0.00625	0.66	3.70	—	50
17	C	300	~0.1	CrO ₃	5.0	0.05	0.93	2.33	—	50
18	C	300	~0.1	CrO ₃	3.75	0.0375	0.52	2.36	—	50
19	C	300	~0.1	CrO ₃	2.5	0.025	0.39	2.21	—	50
20	D	328	0.1	MoO ₃	14.4	0.1	2.95	2.13	—	50
21	B	160	0.05	CrO ₃	1.25	0.0125	0.28	1.63	—	50
22	F	77.65	0.025	CrO ₃	0.625	0.00625	0.37	1.82	—	50
23	G	154	0.05	CrO ₃	1.25	0.0125	0.45	2.00	—	50
24	H	115	0.025	CrO ₃	0.625	0.00625	0.34	0.95	—	50
25	I	304	0.1	MoO ₃	7.2	0.05	1.73	2.27	310	25
26	J	297.6	0.1	MoO ₃	7.2	0.05	1.63	1.25	304	25
27	I	304	0.1	CrO ₃	5.0	0.05	0.18	1.07	340	25
28	J	297.6	0.1	CrO ₃	5.0	0.05	0.44	1.44	304	25

Details of the various intermediates listed in Table I are as follows:—

5	Intermediate A—was prepared in an analogous manner to that of the intermediate in Example II, except that it was prepared as a 50% concentrate in oil.	Intermediate G—the temperature was raised to 200° C and maintained there for 4 hours after which time the mixture was cooled to 120° C and 308 g of mineral oil were added. On filtering, 512 g of product were obtained containing 1.94% nitrogen.	70
10	" B—was prepared in an analogous manner to that of the intermediate in Example I.	" H—was prepared by heating at 200° C for 4 hours a mixture of 218.5 g of polyisobutenyl succinic anhydride of m.w. 1498 (0.1 mole assuming 69.5% purity) and 12.9 g (0.1 mole) of β -(aminoethyl) piperazine. The product was diluted with 230 g of mineral oil to yield 411 g of product containing 0.91% nitrogen.	75
15	" C—was a commercially available additive concentrate of a polyisobutenyl succinimide containing about 2% nitrogen.	" I—was a similar intermediate to A and was prepared in an analogous manner from polyisobutenyl succinic anhydride (MW.1150) and diethylene triamine.	80
20	" D—was a similar intermediate to B prepared in an analogous manner to B but from polyisobutenyl succinic anhydride of MW, about 1150 and the reaction product of pentaethylene hexamine with dicyandiamide.	" J—was a similar intermediate to A and was prepared in an analogous manner from polyisobutenyl succinic anhydride (MW.1150) and triethylene tetramine.	85
25	" E—was a similar intermediate to A and prepared in an analogous manner from a polyisobutenyl succinic anhydride of MW. about 1150 and the reaction product of tetrathylene pentamine and γ -butyrolactone.	" B(1)—The intermediate polyisobutenyl succinic anhydride had a molecular weight of about 1998; otherwise this intermediate was prepared similarly to Intermediate B.	90
30	" F—was prepared by adding 30 g (0.5 moles) glacial acetic acid to a solution of 770 g of intermediate A (neat) in 3 litres of toluene at 70° C and heating under a blanket of nitrogen for 1 hour, after which the solution was gently refluxed under a constant water separator until 10 mls of water were evolved (9 mls theoretical). After this period the toluene was flashed off under vacuum, 776 g of mineral oil added and the mixture heated to 200° C to remove final traces of toluene. After filtration, 1396g of clear product were obtained which contained 1.85% Nitrogen.	" B(2)—The intermediate polyisobutenyl succinic anhydride had a molecular weight of about 808.	95
35		A series of tests was carried out to illustrate the cold sludge dispersant properties in lubricants of the additives of the present invention. A simple laboratory test, designed to obtain information regarding the "cold sludge" dispersant properties of lubricants and additives, was performed in the following manner:—	100
40		A quantity of "cold sludge" was collected from a Lauson engine which had been run deliberately under low temperature conditions using a leaded petrol and, as the lubricant, a plain mineral oil free from additives. This sludge was an emulsion containing from about 10% to about 50% of water, the remainder containing from 0.8—4.0% of lead, from 3—10% of material insoluble in pentane and from 1—10% of material insoluble in benzene, all percentages being by weight. The sludge (1 gram) was shaken for 30 minutes with 20 mls. of a light spindle oil having dissolved therein the additive under test on an auto-	105
45			110
50			115
55	" G—was prepared by adding to 274 g of polyisobutenyl succinic anhydride of MW. about 1150 (0.2 mole of 84% purity) at 90° C, 75.6 g of a 50% solution in water of polyethylencimine of m.w. range 1,000 to 5,000. After stirring for 2 minutes at this temperature		120
60			125
65			130

matic shaking machine and then poured into a measuring cylinder with a tapered base which was allowed to stand in an oven at 60° C.

5 The cylinder was removed from the oven periodically and examined for signs of separation of the sludge. Changes in the colour of the oil proved to be the most reliable indication of sludge separation, the colour changing from black or grey (depending on the sample of sludge used) through brown and speckled (in that order) to that of the clear oil. When the sludge was completely dispersed, the oil was black, blue or grey.

10 Solutions in mineral oil were prepared using the products obtained in examples 1, 2, 3, 4, 5, 6, 8, 10, 11, 13, 16, 18, 19, 21, 22 and 24. The solutions were prepared in such a manner that there was present 2.5% of the neat additive according to the present invention and these gave results comparable to those given by prior art cold sludge dispersants in that the solutions were still black or grey after 4 weeks and in most cases after 25 7 or 8 weeks.

In order to obtain some information on the dispersancy of the additives of the present invention at relatively high temperatures, such as those encountered in the piston ring-belt area of diesel engines, lubricating compositions containing them were subjected to "Panel Coker Tests".

30 In this test the oil sample (250 ml approx) was contained in a sump which was fed by a chicken feed to maintain a constant level of oil. The oil was splashed continuously for 24 hours by means of wires on a rotating spindle on to a heated sloping aluminium panel maintained at 275° C.

The weight change and appearance of the panels were observed after test, the appearance of the panels being assigned merit ratings which were determined by comparing with a set of 28 panels divided into four groups. Where the panels were merely stained these panels were given numbers 1—7 in increasing order of staining, i.e. number 1 was practically clean and number 7 was black. In the second group the same numbers were assigned 1—7 but the suffix "L" was placed after the number to indicate that it had the same staining but was lacquered. Similarly in group 3 the suffix "B" showed the appearance of bubbles on the same background. In Group 4, the suffix "S" showed that the panel was sooted, the number referring to the panel colour. A rating of 4 or less was considered to be reasonable.

The base oil used throughout the test was a solvent refined mineral oil having a viscosity of about 160 secs Redwood I at 140° F and all the blends tested containing 0.9% of a mineral oil concentrate of mixed zinc di alkyl dithiophosphates derived from isopropanol and capryl (1-methyl heptyl) alcohol. This concentrate contained about 8.0% phosphorus.

The results of these tests are given in Table II, from which it will be seen that the additives of the present invention were effective dispersants under high temperature conditions and gave results as good as or better than the basic barium petroleum sulphonate which was a widely used metallic detergent. It has been found by experience that this test, gives results which correlate well with tests in the Petter AV.1 engine when operated under the standard AT—4 conditions.

TABLE II — RESULTS OF PANEL COKER TESTS

Example No.	Product of Example No.	% Additive	Rating	Wt. gain (mg)
Base Oil	—	—	6L	165
Basic barium petroleum sulphonate	—	—	3	28.8
29	1	2	3	41.9
30	2	*	3S	59.5
31	5	1	3	50.8
32	6	2	2L	57.0
33	6	4	4	49.2
34	7	4	4	50.6
35	8	4	3	33.0
36	10	4	3	37.9
37	11	2	2	40
38	12	*	3B	15.6
39	13	1	3	58.2
40	15	4	4B	50.4
41	16	2	3	32.5
42	17	2	3	19.5
43	18	2	2	19.5
44	19	2	2	16.0
45	21	2	3	32.3
46	22	2	3	24.7
47	23	2	4	34.6
48	24	2	3B	34.6

* Percentage of additive was such as to give 1% of the neat material.

Examples of typical fully formulated lubricating oil blends in accordance with the present invention are now given, all percentages being by weight on the weight of the total composition. 5

EXAMPLE 49

Mineral Oil A	28.6%
Mineral Oil B	56.9%
Methacrylate VI Improver (15% solution in mineral oil A)	8%
Additive A	3.7%
ZDDP	0.9%
Additive of Example 19	1.9%

EXAMPLE 50

The composition of Example 50 was substantially the same as that of Example 49 except that the base oil consisted of 85.5% of a mixture of 75% mineral oil B and 25% mineral oil A and the additive of Example 19 was replaced by the additive of Example 13.

Mineral Oil A was a pale spindle oil having a viscosity of about 52 seconds Redwood No. 1 at 140° F.

Mineral Oil B was a solvent refined mineral oil having a viscosity of about 100 seconds Redwood No. 1 at 140° F.

Additive A was the barium salt of a phosphosulphurized polyisobutylene of molecular weight about 1000, the neutralisation having been effected in the presence of an

alkyl phenol, followed by treatment with carbon dioxide.

The Z.D.D.P. was a mineral oil concentrate of a zinc dialkyl dithiophosphate derived from isopropanol and capryl (1-methyl heptyl) alcohol.

The compositions of Examples 49 and 50 were subjected to the Petter W1 and A.V.I. Engine Tests, the results of these tests given in tables III and IV.

In order to evaluate the high temperature oxidation stability of lubricating oils containing additives in accordance with the present invention, tests were carried out in "Petter" (Registered Trade Mark) W-1 engines operating under the following conditions:—

Test duration	36 hours
Speed	1500 \pm 15 r.p.m.
B.H.P.	about 3.3
Sump temperature	280°F.
Coolant outlet temperature	302 \pm 2°F.
Coolant inlet temperature	299 \pm 2°F.
Fuel	PE/IP reference gasoline

The conditions for the Petter W-1 Test are set forth in the Insisture of Petroleum Test IP 176/60T.

In this test the maximum rating for each of the components A, B and C was 10.0, the ratings therefore being merit ratings and not demerit ratings as in the AV-1 test. The general cleanliness of the piston, indicated in the composite rating A+B+C, together with the degree of oxidation of the oil, as adjudged by the corrosion, if any,

of the copper-lead bearings, gave a measure of the oxidation resistance of the oil.

The results of these tests are given in Table III.

In order to evaluate the detergent properties of typical additives in accordance with the present invention at high temperatures, tests were carried out in a Petter (Registered Trade Mark) AV-1 engine, operating under the following conditions (H.A. 1A conditions):

Test duration 120 hours
 Speed 1500 r.p.m.
 B.H.P. 5.0
 Engine cooled with kerosine
 Sump temperature $131^{\circ} \pm 4^{\circ}\text{F.}$
 Coolant outlet temperature 185°F.
 Coolant inlet temperature $173^{\circ} \pm 3^{\circ}\text{F.}$
 Fuel 1.0% Sulphur

The results of these tests are summarised in Table IV.

TABLE III
RESULTS OF PETTER W1 ENGINE TESTS

Blend	Hours Run	Oil Used Per Period (ml)	A Skirt Rating	B Land Rating	C Groove Rating	Under Crown	Oil Ring Rating	A+B+C	Bearing Loss mg.	Small End Bush
Example 49	36	265	9.7	8.0					3	
	72	208	9.9	6.5					10	
	108	115	9.5	4.0	5.3	6.4	9.9	18.8	31	4.5
Example 50	36	150	10.0	9.2					4	
	72	181	9.9	6.5	4.5	6.6	9.9	17.3	12	
	108	174	9.5	3.3					328	4.5
Mineral Oil C	36	217	7.7	2.0	2.1	5.8	9.9	11.8	838	5.5

Mineral Oil C was a solvent refined mineral oil with a viscosity of 160 secs Redwood 1 at 140° F.

5 The results of the Petter W.1 engine test showed that typical fully formulated lubricating oils in accordance with the present invention performed very satisfactorily in this engine even when the duration of the test was extended beyond the normal period of

36 hours to 108 hours, whereas Mineral Oil C gave a very poor result after only 36 hours. Mineral Oil C itself was somewhat more resistant to oxidation than the blends of Mineral Oils A and B used in formulating Examples 49 and 50. Under these test conditions Mineral Oil C inhibited with the zinc dithiophosphate gave A+B+C rating of about 16 at the end of the 36 hour period.

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TABLE IV

RESULTS OF PETTER AV.1 ENGINE TESTS

Demerit 10 = dirty

Blend	A Average ring groove lacquer/ carbon	B Average land lacquer/ carbon	C Skirt Lacquer	A+B+C	Under side lacquer
Example No. 49.	4.7 (3.6)	5.5 (2.5)	0.09	10.3	0.7
Example No. 50	3.2 (2.4)	4.5 (1.5)	0.07	7.8	1.0
Blend X	6.0 (4.0)	5.7 (2.2)	0.5	12.2	3.2

20 Blend X was a commercially available Engine Lubricating Oil.

The results of the Petter AV.1 tests, in which the composite demerit rating A+B+C was the most important criterion, showed clearly that the high temperature dispersancy of Examples 49 and 50 was somewhat superior to that of a commercially available multi-grade motor oil.

WHAT WE CLAIM IS:—

30 1. An oil-soluble chromate or molybdate salt of the reaction product of a long-chain substituted succinic acid or anhydride with a di- or poly-amino compound containing at least one primary amino group, said long-chain substituent being a hydrocarbon group having a molecular weight of at least 700 and said reaction product containing at least one basic nitrogen group.

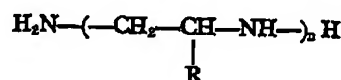
40 2. An oil-soluble salt as claimed in claim 1 wherein the long-chain substituted succinic anhydride is obtained from the reaction between a normally liquid oil-soluble polyolefin having a molecular weight of from 700 to 3000 and maleic anhydride.

45 2. An oil-soluble salt as claimed in claim 2 wherein the polyolefin has a molecular weight of from 750 to 1500.

4. An oil-soluble salt as claimed in claim

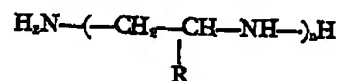
2 or claim 3 wherein the polyolefin is polyisobutylene.

5. An oil-soluble salt as claimed in any one of the preceding claims wherein the di- or poly-amino compound has the formula



where R is H or an alkyl radical having from 1 to 6 carbon atoms and n is an integer of from 1 to 8.

6. An oil-soluble salt as claimed in any one of claims 1 to 4 wherein the di- or poly-amino compound is the reaction product of a polyamine having the formula:—



where n is an integer of from 2 to 8 and R is H or an alkyl radical having from 1 to 6 carbon atoms, with γ -butyrolactone or γ -valerolactone.

7. An oil-soluble salt as claimed in any one of claims 1 to 4 wherein the di- or poly-amino compound is the reaction product of

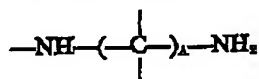
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dicyandiamide with a primary alkylene poly-amine having at least two primary amino groups and containing the group



5 where A is from 2 to 4.

8. An oil-soluble salt as claimed in claim 1 and substantially as hereinbefore described in any one of Examples 1 to 28.

10 9. A process for preparing the oil-soluble salt claimed in any one of the preceding claims which process comprises heating a mixture of an oil concentrate of the reaction product of a long-chain substituted succinic acid or anhydride with a di- or poly-amino compound containing at least one primary amino group, together with chromic or molybdic oxide or acid or ammonium molybdate in the presence of water.

20 10. A process as claimed in claim 9 wherein the mixture is heated to a temperature of from 80° C to 100° C.

25 11. A process as claimed in claim 9 or claim 10 wherein the molar ratio of the succinic acid or anhydride/di- or poly-amino compound reaction product to the inorganic oxide or acid or ammonium salt is from 1:1 to 6:1.

12. A process as claimed in claim 11 wherein the molar ratio is from 2:1 to 4:1.

30 13. A process for preparing the oil-soluble salt claimed in any one of claims 1 to 8 substantially as hereinbefore described in any of Examples 1 to 28.

14. A lubricating composition comprising a

major proportion of a lubricating oil and a minor proportion sufficient at least to provide the desired degree of cold sludge dispersancy and detergency, of the oil-soluble salt claimed in any one of claims 1 to 8. 35

15. A lubricating composition as claimed in claim 14 wherein the proportion by weight of the oil-soluble salt is from 0.5% to 10%. 40

16. A lubricating composition as claimed in claim 15 wherein the proportion by weight of the oil-soluble salt is from 1.0% to 5.0%. 45

17. A lubricating composition as claimed in any of claims 14 to 16 wherein the lubricating oil is a mineral oil of lubricating viscosity.

18. A lubricating composition as claimed in any one of claims 14 to 17 wherein there is also present, as an antioxidant, a minor proportion of a metal salt of a dialkyl or a dialkaryl dithiophosphoric acid. 50

19. A lubricating composition as claimed in claim 18 wherein the antioxidant is the zinc salt of a dialkyl dithiophosphoric acid derived from C₈ to C₁₀ alcohols. 55

20. A lubricating composition as claimed in claim 18 or claim 19 wherein the proportion by weight of the dithiophosphate is from 0.2% to 2%. 60

21. A lubricating composition as claimed in claim 20 wherein the proportion by weight of the dithiophosphate is from 0.5% to 1.5%. 65

22. A lubricating composition substantially as hereinbefore described in any one of Examples 29 to 50.

BOULT, WADE & TENNANT,
111 & 112, Hatton Garden, London, E.C.1,
Chartered Patent Agents,
Agents for the Applicants.

PATENT SPECIFICATION

NO DRAWINGS

1,162,436



**Inventors: SIDNEY JOHN BRANCH, KEITH COUPLAND
and DAVID ANDREW RICHARDSON**

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International Classification:—C 08 f 27/08

COMPLETE SPECIFICATION

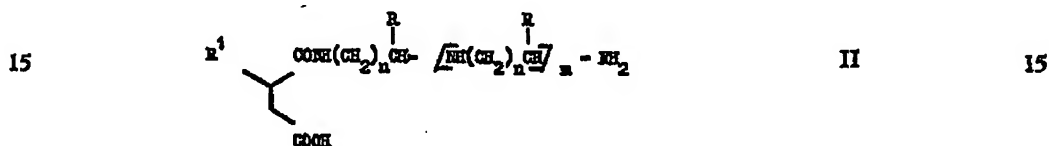
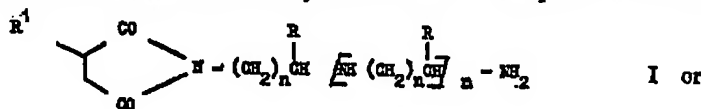
Ashless Dispersants

We, OROBIS LIMITED, of Devonshire House, Mayfair Place, London, W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

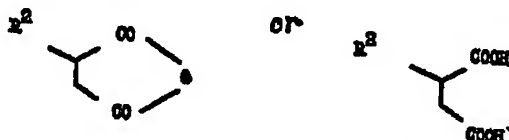
The present invention relates to a process for making certain compounds and their use in lubricant compositions and fuels.

The compounds made by the process of the present invention find use as ashless dispersants, i.e. they will disperse fuel and lubricant oxidation products produced in an internal combustion engine and prevent aggregation of these particles, thus preventing the deposition of carbon and lacquer on engine parts. The compounds are therefore useful as fuel and lubricant additives.

Accordingly the present invention is a process for producing compounds suitable for use as fuel and lubricant additives by the reaction of a compound of formula



with a compound of formula

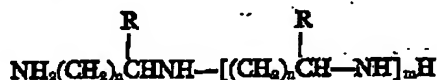


wherein n is zero or an integer and m is zero or an integer, R is hydrogen or an alkyl radical and R¹ and R² are substantially aliphatic hydrocarbon radicals in which either R¹ or R² has a chain length of less than 50 carbon atoms and the arithmetic mean of the chain lengths of R¹ and R² is greater than 50 carbon atoms. The integer n is preferably at least 1.

The compounds I and II may be prepared, for example by the reaction of an alkylene amine with a substantially aliphatic substituted derivative of succinic acid or succinic anhydride, for example a polyalkylene substituted acid or anhydride. It is

preferred to react either equimolar quantities or an excess of the alkylene amine with the succinic acid or anhydride derivative, ratios of amine to succinic acid or anhydride derivative of 1:1 to 1:0.5 being suitable. The product of this reaction is a mixture whose exact composition depends on the reaction conditions employed, but which includes compounds I and II. The reaction requires heating, for example to a temperature between about 80°C and 200°C. It is preferred to use a temperature above 100°C to remove water produced during the reaction. The reaction may be carried out in the presence of a diluent oil or a solvent. Solvents which will form azeotropes with water, for example, toluene, are preferred. Nitrogen may also be blown through the mixture to expel water.

The alkylene amine is a compound of formula



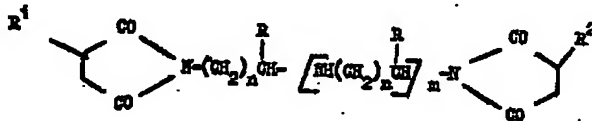
where n, m and R are as defined above. The radical may contain up to 6 carbon atoms and is preferably hydrogen or a methyl radical. Suitable compounds include ethylene diamine, when m is zero, n is 1 and R is hydrogen; 1,2-propylene diamine when m is zero, n is 1 and R is methyl; and 1,3-propylene diamine when m is zero, n is 2 and R is hydrogen. Other examples of suitable compounds are diethylene triamine, triethylene tetramine, tetraethylene pentamine, tri-1,2-propylene tetramine, tri-1,3-propylene tetramine and octaethylene nonamine, i.e. m may suitably have values up to 9.

The compound I or II, or a mixture of compounds I and II is reacted with a quantity of a substantially aliphatic substituted derivative of succinic acid or succinic anhydride to give the desired reaction product. The substantially aliphatic substituent is preferably a polyalkylene radical. The amounts of compound I and/or II and polyalkylene derivative of succinic acid or anhydride used are not critical. The molar ratio of compound I and/or II to succinic acid or anhydride derivatives used depends upon the amine employed but preferably lies in the range 0.5:1 to 2:1. The reaction may be carried out under conditions described above for the preparation of compounds I and II.

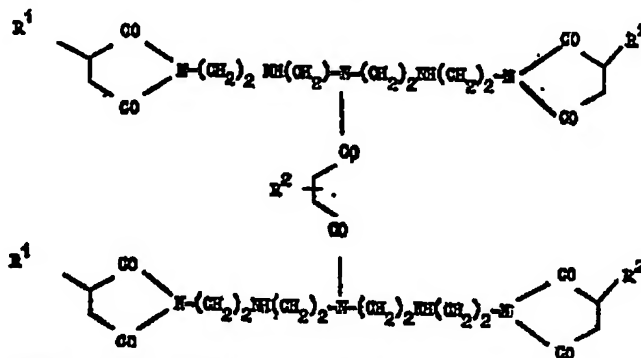
The substituted succinic acids and anhydrides used in these reactions may be obtained by the reaction of an olefin, alkyl chloride or alcohol with maleic anhydride. The compound which is reacted with maleic anhydride is frequently derived from polymers or copolymers of, for example, ethylene, propylene or butylene. These compounds which are commercially available are not in fact single compounds of a definite chain length but mixtures of compounds, and the chain length quoted is the average chain length of the compounds in such a mixture. Where appropriate, reference to the chain length of a substituent is to be understood as reference to the average chain length of a mixture of substituents.

The chain length of either R¹ and R² is less than 50 carbon atoms, preferably in the range 12 to 49. The chain length of the other radical is greater than 50 and preferably less than 250 carbon atoms, the range being preferably 50 to 100. The length is sufficient to raise the arithmetic mean length of the chain lengths R¹ and R² to greater than 50. A radical having a chain length of 70 carbon atoms is particularly suitable for use in the process of this invention.

It is believed that the products obtained by the process of this invention have the following structure, but is not known with certainty.



In the case where the compound I or II contains more than one free amine group, for example when the alkylene amine used in its production is a polymer such as tetraethylene pentamine, and it is reacted with an excess of substituted succinic acid or anhydride, a compound whose structure is believed to be the following may be obtained.



The invention is illustrated in the following example.

EXAMPLE

Tetraethylene pentamine (150 g.) was warmed to 50°C and polyisobutyl succinic anhydride (Mwt 760, 47 carbon atoms in the side chain) as an oil solution (1614 g.) added slowly with vigorous agitation. The temperature was raised to 150°C. and a stream of nitrogen passed through the solution to void expelled water. The resultant intermediate was cooled to 100°C and polyisobutyl succinic anhydride (Mwt=1200, 78 carbon atoms in the side chain) in oil solution (1650 g.) added. The temperature was raised to 150°C and held at this temperature for 1 hour. To expel all the water of reaction the reactants were further heated to 180°C for 1 hr at reduced pressure. The product, a brown clear oil solution, had a nitrogen content of 1.6%.

The product of the Example was evaluated in the Petter A.V. 1 diesel engine run to Ministry of Defence Specification DEF 2101D. (Petter is a registered Trade Mark). The test blend consisted of the product of the Example (1.03%) + calcium phenate (29 mM) + zinc dialkyl dithiophosphate (8mM) in which the alkyl groups were derived from a mixture of C_4 and C_6 alcohols, in solvent Refined High VI Middle East Stocks blended to SAE 30.

By the symbol "mM" is meant millimoles of active metal present per kilogram of finished lubricant.

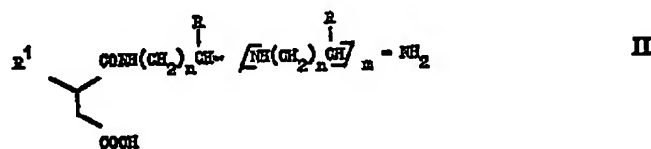
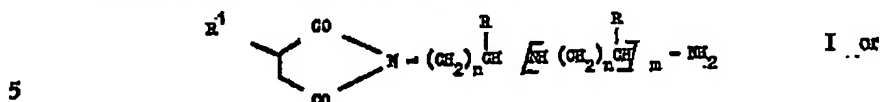
The result is given in the following table.

Component	Possible Rating	Actual Rating	Acceptable Limit
Groove 1	10	5.5	<5
2	10	8.5	"
3	10	7.0	"
4	10	8.7	"
Land 1	10	5.1	"
2	10	7.3	"
3	10	6.7	"
Average Ring groove and Land merit	10	6.9	7
Skirt Exterior	10	9.95	"
Skirt Interior	10	9.4	"
Overall Rating	80	59	>55

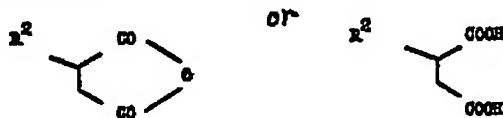
The Acceptable limit is a guide line issued by the Ministry of Defence.

WHAT WE CLAIM IS:—

1. A process for producing compounds suitable for use as fuel and lubricant additives by the reaction of a compound of formula



with a compound of formula



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wherein n is zero or an integer and m is zero or an integer, R is hydrogen or an alkyl radical, R¹ and R² are substantially aliphatic hydrocarbon radicals in which either R¹ or R² has a chain length of less than 50 carbon atoms and the arithmetic mean of the chain length of R¹ and R² is greater than 50 carbon atoms.

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2. A process according to claim 1 wherein the integer n has the value 1 or 2.

3. A process according to claims 1 or 2 wherein the integer m has the value 1 to 9.
4. A process according to any of the preceding claims wherein R is an alkyl radical having up to 6 carbon atoms.
5. A process according to claim 4 wherein R is a methyl radical.
- 5 6. A process according to any of the preceding claims wherein the compound of formula I or II is prepared by reaction of an alkylene amine with a polyalkylene substituted derivative of succinic acid or anhydride.
- 10 7. A process according to claim 6 wherein the alkylene amine is ethylene diamine; 1,2-propylene diamine, 1,3-propylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, tri-1,2-propylene tetramine, tri-1,3-propylene tetramine or octaethylene nonamine.
8. A process according to claim 6 or 7 wherein the reaction is carried out at a temperature in the range 80°C to 200°C .
- 15 9. A process according to claim 8 wherein the reaction is carried out above 100°C .
10. A process according to any of claims 6 to 9 wherein the reaction is carried out in the presence of a solvent which will form an azeotrope with water.
11. A process according to claim 7 wherein the solvent is toluene.
12. A process according to any of the preceding claims wherein the molar ratio of compound I and/or II reacted with the substituted succinic acid or anhydride lies in the range 0.5:1 to 2:1.
- 20 13. A process according to claim 12 wherein the reaction is carried out at a temperature in the range 80° to 200°C .
14. A process according to claim 13 wherein the reaction is carried out above 100°C .
- 25 15. A process according to any of claims 12, 13 or 14 wherein the reaction is carried out in the presence of a solvent which will form an azeotrope with water.
16. A process according to claim 15 wherein the solvent is toluene.
17. A process according to any of the preceding claims wherein the chain length of either R^1 or R^2 is in the range 12 to 49 carbon atoms.
- 30 18. A process according to claim 17 wherein the chain length of the radical which is not in the range 12 to 49 carbon atoms is in the range 50 to 250 carbon atoms.
19. A process according to claim 18 wherein the chain length of the radical is in the range 50 to 100 carbon atoms.
- 35 20. A process for producing compounds suitable for use as fuel and lubricant additives substantially as herein described with particular reference to the Example.
21. Compounds produced by the process of any of the preceding claims.
22. Fuels or lubricants containing any of the compounds claimed in claim 21.

MICHAEL W. PREUVENIERS,
Agent for the Applicants,
Great Burgh, Epsom, Surrey.